Driven Diffusion in Periodic Potentials with Stochastic Path Integral Hyperdynamics

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We consider the driven diffusion of Brownian particles in 1D periodic potentials using the recently proposed Stochastic Path Integral Hyperdynamics (SPHD) scheme [L.Y. Chen and L.J.M. Horing, J. Chem. Phys. **126**, 224103 (2007)]. First, we consider the case where a single Brownian particle is moving in a spatially periodic potential and subjected to an external ac driving force. We confirm that there is no stochastic resonance in this system and find that at higher frequencies the diffusion coefficient D is strongly suppressed. The second case is that of a dimer moving in a periodic potential with a static bias. For this case, there's a strong suppression of D when the dimer bond length is an integer multiple of the lattice constant of the potential. For both cases, we demonstrate how the SPHD allows us to extract the dynamical information exactly at different bias levels from a single simulation run, by calculating the corresponding statistical re-weighting factors.

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INTRODUCTION

The study of particles performing Brownian motion in a periodic potential constitutes a hallmark example of stochastic particle dynamics with important applications in various branches of science and technology. Perhaps the most common application of periodic Brownian motion is the diffusive dynamics of atoms and molecules on crystal surfaces [1]. Surface diffusion is among the most important mechanisms that controls processes such as island nucleation and subsequent surface growth. It has been shown that by controlling the mobility of particles on the surface by external means, such as an ac or dc electric field, allows morphological control over the growing surfaces [1]. It is thus of great interest to model periodic Brownian motion with static and time-dependent external fields.

To this end, there have been several studies reporting the diffusion of a single Brownian particle in a periodic potential with external ac bias applied [2, 3, 4, 5]. The case of a dimer consisting of two connected particles has also been considered [6, 7, 8], in which case there's an additional length scale in the problem, namely the dimer bond length, as shown schematically in Fig. 1. Most of the studies reporting the behavior of Brownian particles discuss the influence of an oscillating bias on transport coefficients. The central issue here is existence of a stochastic resonance (SR), which can greatly enhance the diffusion coefficient D in 2D [3]. However, it has been shown in the case of 1D periodic potentials that although the local jump rate of particles can be enhanced, there is no true SR in the hydrodynamic limit [2, 5]. An interesting limit of the periodic Brownian motion is where the energy barrier V_0 is much larger than the thermal energy, *i.e.* $\beta V_0 \gg 1$ [1], where $\beta = 1/k_B T$ and k_B is the Boltzmann constant and T the temperature (cf. Fig. 1). Since Brownian motion is activated by thermal fluctuations, the diffusion rate is proportional to $\exp(-\beta V_0)$ which becomes very small at low temperatures. To overcome this rare event problem in Molecular Dynamics (MD) simulations, Voter [9] has proposed the so-called Hyperdynamics (HD) scheme, which involves accelerating the dynamics by adding proper bias potential, which effectively lowers the barrier height. The dynamics is then corrected based on the approximate Transition State Theory (TST). There exist various approaches to the choice of the bias potential, and some examples can be found in Refs. [11, 12, 13, 14].

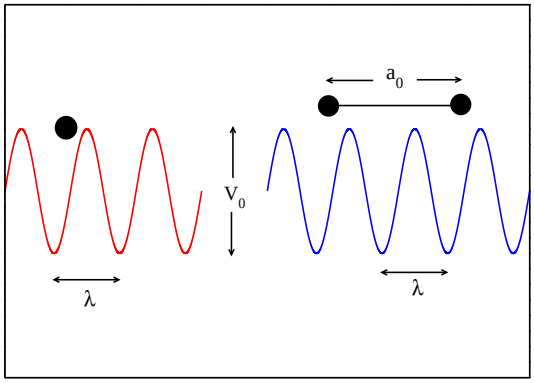

FIG. 1: Driven diffusion in a 1D periodic potential. The relevant parameters are the barrier height V_0, the lattice constant λ and the dimer bond length a_0. The details of an external bias are discussed in the text.

However, recently a new scheme has been proposed that is based on the mapping of the stochastic Langevin equation to a path integral form [10]. Unlike the standard HD scheme, this so-called Stochastic Path Integral Hy-

perdynamics (SPHD) method allows an *exact* correction of the dynamics by resampling the simulated paths. In other words, this method is not restricted to the TST approximation. Further, it is not restricted to static energy barriers; both entropic barriers and even time-dependent bias can be employed. This allows an efficient way to overcome the large barrier problem, as demonstrated in Ref. [10]. However, the SPHD method is not limited to the case of high barriers. Since in principle any external bias force can be used, it should be possible to obtain results for *many different bias values* from running LD simulations with a single value of the bias force, or even without such a force if need be. To demonstrate this, in this work we have undertaken to employ the SPHD method to study periodic Brownian motion for two interesting cases. In the first case, we consider the diffusion of a single Brownian particle in a 1D periodic potential with ac forcing. The second case is that of a dimer diffusing in a 1D periodic potential with a static bias. For both cases, we show how the SPHD method can be efficiently employed to obtain the transport coefficients for a range of different external forcing terms from single simulation runs.

STOCHASTIC PATH INTEGRAL HYPERDYNAMICS

Brownian motion of a single particle can be represented by the Langevin equation

$$m\ddot{r}(t) + m\gamma\dot{r}(t) - F = \xi(t), \tag{1}$$

where $r(t)$ denotes the position of the particle (of unit mass m) at time t, moving under the influence of external force F and the random noise term $\xi(t)$ satisfies $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = 2k_BTm\gamma\delta(t-t')$, where γ denotes the friction coefficient. In general, to accelerate the dynamics one must add a bias force $F_b(r,t)$ to the Langevin equation to get

$$m\ddot{r}(t) + m\gamma\dot{r}(t) - F - F_b(r,t) = \xi(t). \tag{2}$$

With an appropriately chosen bias potential, the dynamics of the system evolves much faster than in the original Langevin equation. The dynamics given by numerically solving Eq. (2) is fictitious, of course. However, the use of path integral formalism allows an exact compensation of the effect of adding the bias force by defining an effective action functional $I_\xi(t)$ [10]

$$I_\xi(t) = \frac{1}{4\gamma}\sum_i -F_b(r,t_i)\left[-F_b(r,t_i) - 2\xi(t_i)\right]\Delta t. \tag{3}$$

This expression constitutes time integration for a given realization of the random noise force ξ along a given trajectory $r(t)$. To recover true dynamics in the absence of $F_b(r,t)$, one has to estimate the SPHD statistical weight factor $\exp(-\beta I_\xi)$ and simply use it to re-weight every sampled trajectory.

The fundamental quantity associated with Brownian dynamics is the single-particle (tracer) diffusion coefficient [1], which can be defined through the mean square displacement (MSD) of the tracer particle as

$$D = \lim_{t\to\infty}\frac{1}{2t}\langle[r(t)-r(0)]^2\rangle. \tag{4}$$

When studying particle diffusion the mean square displacement (MSD) at zero bias (true dynamics) can be obtained by running SPHD with a bias, calculating $I_\xi(t)$ along every trajectory and re-weighting as

$$\left\langle[r(0)-r(t)]_0^2\right\rangle = \left\langle[r(0)-r(t)]_{HD}^2\, e^{-\beta I_\xi}\right\rangle, \tag{5}$$

where the subscripts 0 and *HD* correspond to the quantities with zero bias (true dynamics) and finite bias, respectively. The SPHD has an additional powerful feature which can be seen from the biased Langevin equation and the expression for the re-weighting factor $I_\xi(t)$. It is possible to obtain the true dynamics for *any* value of the bias force $0 \le f_b \le F_b$ by estimating $I_\xi(t, f_b)$ corresponding to some f_b. With this, the true dynamics at multiple bias levels (f_b) can be extracted, simultaneously, from a single simulation run of biased dynamics according to Eq. (2) and estimating the weight factors, corresponding to multiple values of f_b along all the trajectories.

RESULTS AND DISCUSSION

Brownian Particle in Periodic Potential with Time-Varying Bias

The first case where we consider the application of the SPHD method is that of a Brownian particle in a one-dimensional spatially periodic potential with an external, time-dependent ac driving force [2, 3, 4, 5]. For such a system, the equation of motion is given by

$$m\ddot{x}(t) + m\gamma\dot{x}(t) - F = \xi(t) + A\sin(2\pi\omega t), \tag{6}$$

where the second term on the right hand side indicates an ac driving force with amplitude A and frequency ω. The diffusion of a Brownian particle can be studied with respect to various values of these two parameters. F is force due to spatially periodic potential $-(V_0/2)[1-\cos(2\pi x/\lambda)]$. Here, we have employed the SPHD method by numerically solving Eq. (6) with $A = 0$ using the standard velocity Verlet scheme [15]. The diffusion coefficients for different values of A and ω can be obtained by choosing $f_b(A,\omega) = A\sin(2\pi\omega t)$ and then estimating the correction factor $I_\xi(t, f_b)$ and the reweighing factor $\exp(-\beta I_\xi)$ for every bias force.

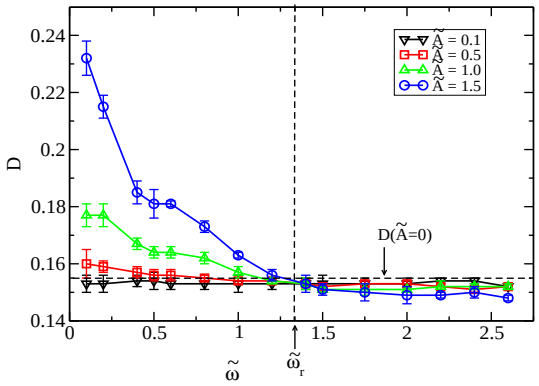

FIG. 2: Diffusion coefficients for the ac-driven Brownian particle in a periodic potential as a function of the driving frequency $\tilde{\omega}$ for various values of the amplitudes $\tilde{A}$. The horizontal dashed line shows the reference value of D for $\tilde{A} = 0$, and the vertical dashed line indicates the position of the resonance frequency $\tilde{\omega_r}$ (see text for details). The solid lines are just guide to an eye and contain no other significance.

We set scales for length $= \lambda$, energy $= k_BT$ and mass $= m$. Then time unit is defined as $t = \lambda\sqrt{(m/k_BT)}$ and all other relevant quantities are expressed as dimensionless and indicated by a tilde over the respective symbols.

The parameters we have used in the present work are $\tilde{V_0} = 2$, and $\tilde{\gamma} = 2$. The time step we have chosen is $\Delta\tilde{t} = 0.0005$ [16]. From the unbiased runs (in this case with $\tilde{A} = 0$) we have computed the MSD and the corresponding diffusion coefficients as given in Eq. (4) for a range of values of $\tilde{A}$ ($\tilde{A} = 0.1, 0.5, 1.0, 1.5$) and the frequency, as summarized in Fig. 2. All the data have been averaged over 10^6 trajectories. Our results demonstrate that for a given amplitude $\tilde{A}$ of the external ac driving force, D decreases monotonically with the frequency $\tilde{\omega}$. For higher values of $\tilde{\omega}$ studied, it appears that large values of amplitude $\tilde{A}$ lead to a lower D than small values of $\tilde{A}$. It seems that the ac bias for higher values of both $\tilde{A}$ and $\tilde{\omega}$ acts detrimental to activation in the diffusive motion. This feature can be effectively used to localize the motion of the particle.

It is of interest to compare the SPHD with direct simulations for the Langevin equation. In this case, a larger time step of $\Delta\tilde{t} = 0.005$ was sufficient, and averages were taken over 10^6 trajectories. In Table I we show results for the case of $\tilde{\omega} = 0.2$ as a function of increasing amplitude $\tilde{A}$. We find excellent agreement between these data. For the highest value of $\tilde{A}$, studied here, it appears that SPHD gives a slightly smaller estimate of D than the LE, although the data still agree within the error bars. Our preliminary results indicate that with increasing bias path sampling should be increased, too, which is caused by the exponential decrease in the reweighing factor with increasing $\tilde{A}$.

TABLE I: Values of the diffusion coefficient D from SPHD and direct solution of Eq. (6) with $\tilde{\omega} = 0.2$.

$\tilde{A}$	D (from Eq. (6))	D (SPHD)
0.1	0.155 ± 0.001	0.153 ± 0.002
0.5	0.163 ± 0.002	0.159 ± 0.004
1.0	0.185 ± 0.003	0.178 ± 0.005
1.5	0.225 ± 0.003	0.215 ± 0.007

An interesting issue in Brownian motion under time-periodic forcing concerns the existence of stochastic resonance, which leads to a significant enhancement of the relevant transition rates [5]. In the case of a double-well potential, SR is expected to occur in the vicinity of the matching condition $\omega_r = \pi r_e$, where r_e is the (thermal) escape rate [5]. In the case of an extended periodic potential there's enhanced escape for local diffusion jumps over the barrier V_0 [2]. However, it has been shown in Refs. [2, 3, 5] that this enhancement exactly cancels out in the hydrodynamic limit for a 1D periodic potential such as used in the present study. One can estimate the frequency (ω_r) as [5]

$$\tilde{\omega_r} = (\frac{\pi^2\tilde{V_0}}{\tilde{\gamma}})e^{-\tilde{V_0}} \tag{7}$$

The calculation results in $\tilde{\omega_r} = 1.336$. As mentioned above, there is no peak in the value of D around $\tilde{\omega_r}$ which confirms the absence of stochastic resonance.

Brownian Dimer in Tilted Periodic Potentials

The second case that we consider here is that of a Brownian dimer diffusing along a tilted 1D periodic potential (cf. Fig. 1). The equations of motion for the beads are given by

$$m\ddot{x}_i(t)+m\gamma\dot{x}_i(t)-F = \xi_i(t)-\nabla_{x_i}[\frac{V_0}{2}(1-\cos(2\pi x_i/\lambda))-b_t x_i], \tag{8}$$

where $i = 1, 2$ and the variables $x_i(t)$ denote the positions of the two beads. The second term on right hand side denotes the force associated with external static bias with spatial periodicity λ (see Fig. 1) and tilt b_t. On the left hand side, F represents the force due to the interaction between the constituent monomers of the dimer which is given by a combination of the Lennard-Jones (LJ) potential and the FENE (Finitely Extensible Nonlinear Elastic) potential. The LJ potential is given by

$$\begin{aligned} U_{LJ}(r) &= 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon, \text{for } r \le 2^{1/6}\sigma; \\ &= 0, \quad \text{otherwise.} \end{aligned} \tag{9}$$

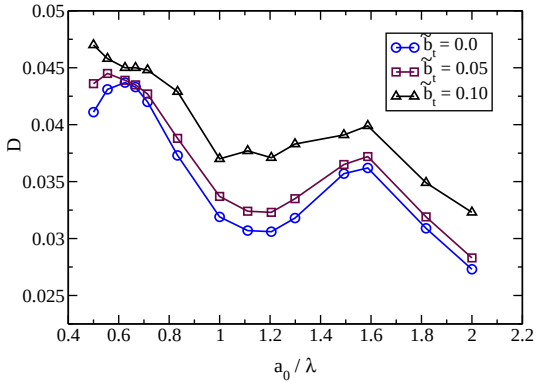

FIG. 3: The dimer diffusion coefficient D *vs.* the wavelength a_0/λ for various tilts. Error bars are of the order of the size of the symbols, or smaller. The solid lines are just guide to an eye and contain no other significance.

Here, ε and σ define the energy and length scales, respectively, and r is the separation between the monomers. The FENE potential is given by

$$U_{FENE}(r) = -\frac{1}{2}kR_0^2 \ln(1 - r^2/R_0^2), \qquad (10)$$

where k is the effective spring constant and R_0 sets the maximum allowed separation between the monomers.

The SPHD method was employed by numerically integrating Eq. (8) corresponding to a spatially periodic surface with given λ and zero tilt. The dynamics along tilted periodic potentials was recovered by setting $f_b(b_t) = -\nabla_{x_i}[-b_t x_i]$. For the resampling, the corresponding weight factors were evaluated as in the previous section.

Again, we set scales for length $= \sigma$, energy $= \varepsilon$ and mass $= m$. Then time unit is defined as $t = \sigma\sqrt{(m/\varepsilon)}$ and all other relevant quantities are expressed as dimensionless and indicated by a tilde over the respective symbols.

The parameters were set to be $\tilde{V}_0 = \tilde{T} = 0.1$, $\tilde{\gamma} = 1$ and the time step $\Delta\tilde{t} = 0.0005$, with averages taken over 10^6 trajectories. The FENE parameters are $\tilde{k} = 1$ and $\tilde{R}_0 = 2$. The periodicity of the 1D potential was changed between $\tilde{\lambda} = 1/2$ and 2, and the tilt parameters were $\tilde{b_t} = 0.0, 0.05, 0.1$. The effective diffusion coefficient was estimated by using the relation

$$D = \lim_{t\to\infty} \frac{\langle x_{\rm cm}^2(t)\rangle - \langle x_{\rm cm}(t)\rangle^2}{2t}, \qquad (11)$$

where $x_{\rm cm}$ is the center of mass of the dimer, in order to subtract the drift term caused by $\tilde{b_t} > 0$. In Fig. 3 we summarize our results for D as a function of the wavelength of the periodic potential for three tilt values. For the case of a dimer, there are now two relevant length scales in the system (see Fig. 1): the zero temperature equilibrium bond length of the dimer $\tilde{a_0} \approx 1.10$ and the wavelength $\tilde{\lambda}$ of the underlying periodic potential. Thus, for the dimer motion there's a matching of the two lengths when the ratio $a_0/\lambda = n$ is an integer. On the other hand, when this ratio is a half-integer, there's strong competition between the dimer bond and potential energy. In the latter case, it should be easier for the dimer to escape as the effective diffusion barrier is lower. Indeed, as seen in Fig. 3 we find that for every value of the tilt there is a strong decrease in D in the vicinity of the first matching condition $a_0/\lambda = 1$ [17]. On the other hand, near $a_0/\lambda = 3/2$ there is a local maximum in D, as expected, followed by another pronounced minimum near $a_0/\lambda = 2$. In our model, the interaction between the monomers is highly anharmonic. This results in an equilibrium dimer separation which is temperature dependent and the first minimum in D in Fig.3 is shifted from the zero temperature value $a_0/\lambda = 1$ to $a_0/\lambda = 1.2$. A finite tilt increases the overall magnitude of D while its non-monotonic behavior as a function of a_0/λ prevails almost unchanged . Our results are consistent with the Langevin dynamics studies of Bammert *et al.* [6], who considered dimer diffusion in a 2D periodic square potential (with a hydrodynamic interaction term included) and found that there's a local maximum in D for $a_0/\lambda = 3/2$. Heinsalu *et al.* [7] have reported dimer diffusion on a 1D washboard-like potential, and they also find a flat minimum at $a_0/\lambda = 1$ for small tilts.

Another interesting feature in our results is that the minima in D deepen with increasing n. This can be understood as follows. When the matching condition is met (*i.e.* n is an integer), both beads in the dimer can sit exactly at the minima of the potential separated by $n-1$ minima. The elementary diffusion move of the dimer (local jump rate) consists of both of the beads crossing the saddle points (potential maxima) synchronously (assuming that bond fluctuations can be neglected). For every n the effective diffusion barrier is exactly the same independent of n. However, the jump length of the dimer depends on n (in units of $\tilde{a_0}$) such that the distance the dimer moves is given by $\tilde{a_0}/n$. Thus, if we use the Dynamical Mean Field theory to approximate the diffusion coefficient [18], the prefactor of D is proportional to the jump length squared, which gives

$$D \propto \frac{1}{n^2}. \qquad (12)$$

We have analysed the data upto around $a_0/\lambda = 4$ and checked that minima of D near integer values of a_0/λ indeed decreases with increasing n, but slower than predicted by Eq. (12) for the present set of parameters. Indeed, Eq. (12) strictly holds only in the limit of a rigid dimer bond and $\tilde{V}_0 \gg 1$, which is not in the range of the parameters used here.

In analogy to the single particle case, we have compared our results from the SPHD scheme to data obtained from directly integrating the Langevin equation

TABLE II: Comparison between results for the diffusion coefficient D obtained from SPHD and from Eq. (8) with tilt $\tilde{b_t} = 0.10$.

a_0/λ	D (Langevin eq.)	D (SPHD)
1/2	0.0482 ± 0.0004	0.0470 ± 0.0005
2/3	0.0454 ± 0.0005	0.0450 ± 0.0004
1	0.0368 ± 0.0003	0.0370 ± 0.0004
3/2	0.0393 ± 0.0004	0.0391 ± 0.0006
2	0.0320 ± 0.0004	0.0323 ± 0.0006

with the static bias for the largest value of the tilt $\tilde{b_t} = 0.10$, for various values of $\tilde{\lambda}$. For the straight LD simulations $\Delta\tilde{t} = 0.005$ and averages were taken over 10^6 trajectories. There is again good agreement between these two sets of data.

An intriguing further extension of the SPHD method is extrapolation with more than one bias force parameter. In the present case, we did some test runs by numerically integrating Eq. (8) corresponding to a flat surface *and* zero static bias ($V_0 = b_t = 0$). The dynamics along tilted periodic potentials was recovered by setting $f_b(\lambda, b_t) = -\nabla_{x_i}[(V_0/2)(1-\cos(2\pi x_i/\lambda)) - b_t x_i]$, and we used the same parameters as in the single-parameter resampling case. We found that using 10^6 trajectories the discrepancies with respect to the data in Table II were about 16 % at largest. This is due to the fact that when simulations are run on a smooth surface, all trajectories of the dimer are weighted equally. However, in the actual periodic potential the main contribution to the diffusion coefficient comes from paths crossing the saddle point from one minimum to another. Thus, in the resampling procedure most of the paths are not relevant for determining the value of D, and thus the errors remain relatively large even with 10^6 paths for the present case.

SUMMARY AND CONCLUSIONS

In this work, we have employed the recently proposed SPHD scheme to study the diffusive motion of Brownian particles in periodic potentials in 1D. Unlike the HD schemes proposed so far, the SPHD scheme allows an exact correction of the biased dynamics based on reweighing of all the transition paths. There's also no restriction for the type of bias potential used, and thus the SPHD method can be used to extrapolate results to *multiple* values of the bias force from a single simulation run, as shown by the two cases we have studied here: time-dependent forcing for a single Brownian particle and constant forcing for a Brownian dimer. For a Brownian particle in an external ac bias, our results are in agreement with previous studies and show that there's no stochastic resonance in this system. For the second case of a dimer moving in a periodic potential with a static bias we find a strong suppression of D when the dimer bond length is an integer multiple of the lattice constant of the potential. This suppression is weakened by an applied dc bias. Our work demonstrates how external forcing can be used to control particle mobilities in periodic potentials.

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